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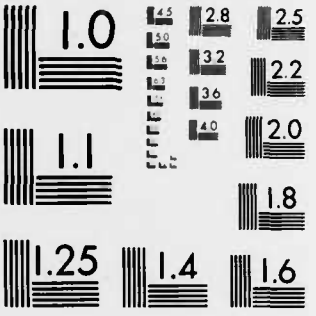

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Study of Strong Electrolytes by X-ray Spectroscopy at the Cl K-Edge

by

Donald R. Sandstrom

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Chlorine Cl K-edge X-ray absorption spectra were measured for non-stoichiometric transition metal chloride solutions. Results confirm the degree of detail of cation-anion association available from both the XANES and EXAFS spectral regions.

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Proposal No. 721M

STUDY OF STRONG ELECTROLYTES BY X-RAY SPECTROSCOPY AT THE Cl K-EDGE

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X-ray absorption measurements carried out during the January, 1983, run have extended measurements of the Cl K-edge spectra of aqueous solutions to non-stoichiometric transition metal chloride solutions. Chloride solutions containing excess chloride ions from both HCl and LiCl were examined. Solutions containing excesses of the same metal ions were prepared by addition of the corresponding metal nitrate. Analysis of these results is in progress, and detailed comparison with results measured earlier for stoichiometric solutions under proposal No. 553M cannot yet be made. However, the present results confirm the general observation made earlier that considerable detail about the degree of cation-anion association can be deduced from both the XANES and EXAFS regions of the absorption spectra.

The detail that can be obtained from the Cl K-edge spectra is illustrated most clearly by results of analysis of the series of $FeCl_3$ solutions measured earlier. Several spectra were measured in the concentration range from 0.40 to 5.75 moles/liter. The spectrum of hydrated $FeCl_3$ crystals was also measured. The XANES portion of the spectra all show a strong single pre-edge peak, shown in Figure 1. A similar feature is also present in other transition metal chloride salts and solutions, but not in the spectra of alkali and alkaline earth metal chlorides. It is believed to be associated with transitions to an *unfilled* orbital derived from the metal 3d and chlorine 2p states.[1] As shown in Figure 1, its intensity is very concentration dependent, and approximates the variation in the degree of anion-cation coordination expected over this concentration range.[2] This feature of the Cl K-edge spectra is in marked contrast to Fe K-edge spectra of the same solutions, for which the corresponding pre-edge peak is very weak. The difference in oscillator strengths is believed to reflect the different symmetry environments of the Fe vs Cl ions in the solution complexes.

Fourier transforms of EXAFS spectra for the same series of solutions are shown in Figure 2. The contributions of Fe and O backscatterers are well separated and clearly show an increase in the relative degree of Cl-Fe bonding compared to the degree of Cl-O bonding with increasing concentration, in agreement with the trend seen in the XANES results.

Pre-edge features similar to that of the $FeCl_3$ spectra are also visible in the results for $NiCl_2$ and $CuCl_2$ solutions. Because of the apparent sensitivity to relatively small degrees of cation-anion bonding, information from the XANES should be especially useful in the study of cases such as $NiCl_2$ solutions, where EXAFS and X-ray scattering have been unable to detect direct Ni-Cl bonding.[3]

Work supported by Office of Naval Research.

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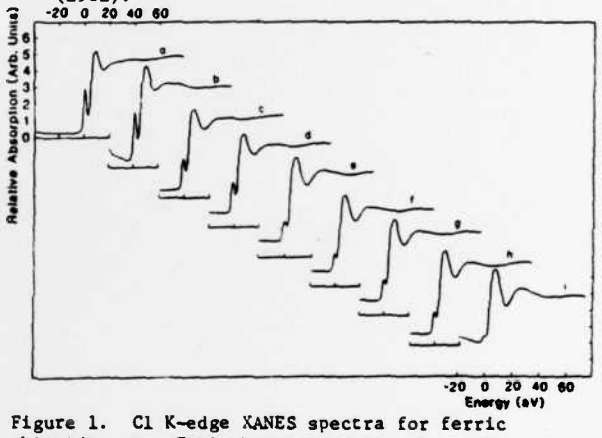

Figure 1. Cl K-edge XANES spectra for ferric chloride. a. $FeCl_3$ hydrated salt. b. - i. $FeCl_3$ aqueous solutions in order of decreasing Fe_{3+} concentration in range 5.75 - 0.40 moles/liter.

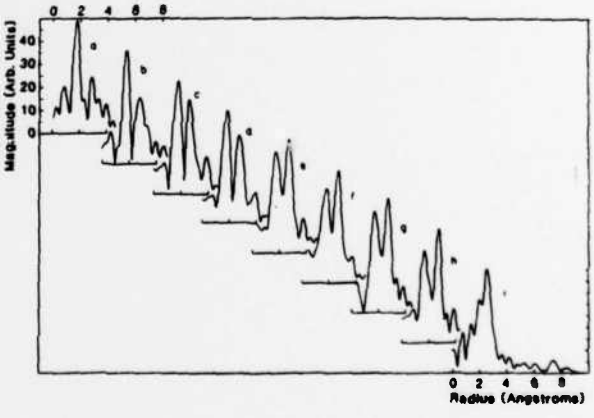

Figure 2. Fourier transforms of Cl K-edge EXAFS spectra for same ferric chloride hydrated salt and solutions as Figure 1.

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